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HAZARDS FROM CHLORATES AND PERCHLORATES IN MIXTURES WITH REDUCING MATERIALS

BY

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HAZARDS FROM CHLORATES AND PERCHLORATES IN MIXTURE WITH REDUCING MATERIALS[1]

By Irving Kabik[2]

INTRODUCTION

Chlorates and perchlorates, when mixed with certain reducing materials, may give a detonating explosive of considerable power. Concerning explosive chlorate mixtures, Guttman[3] states that they "have at all times fascinated inventors on account of the large amount of oxygen stored up in potassium chlorate, which can be given off so readily. When Lavoiser and Berthollet tried to make a chlorate powder in a stamp mill in 1788, they made a great show of it, and even two ladies were present. Unfortunately, after a certain amount of pounding the powder exploded and killed an official and the daughter of the Government commissary, who assisted at the experiments.***. It is interesting to observe how the same old mixtures are proposed over and over again with slight alterations only, in order to qualify for a patent. Potassium chlorate with some carbonaceous matter like charcoal, sugar, starch, glycerin, flour, or sometimes a vegetable or mineral oil and the like occurs again and again."

Sprengel explosives, in which some of the undesirable sensitivity of the chlorate was minimized by coating the crystals with a liquid reducing agent, received some attention after a patent was issued to Dr. Herman Sprengel in England in 1871.[4] A somewhat similar explosive, known as Rack-a-

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7340."

[2] Chemical engineer, Eastern Experiment Station, Bureau of Mines, College Park, Md.

[3] Guttman, Oscar, Twenty Years' Progress in Explosives: Smithsonian Report for 1908, p.267.

[4] British Patents 921 and 2642 of 1871.

Rock, was patented in the United States by Silas R. Divine in 1881.[5] In a class of explosives known as the Steelites, the chlorate is encased in oxidized resin.[6]

In the United States, such explosives have had only a relatively short commercial life in competition with nitrate types. During a war, when explosives are in heavy demand and raw material supplies are short, renaissance of such mixtures is to be expected. Following the present war considerable quantities of chlorates and perchlorates will be available. Promoters may seek to market explosives containing these ingredients, and studies probably will be made to develop such explosives with improved characteristics.

The Bureau of Mines receives inquiries from time to time concerning the properties of chlorates and perchlorates, and the present summary has been written to supply information of interest.

COMMENTS ON THE SENSITIVITY OF CHLORATE MIXTURES

According to Gody,[7] "The mixture of combustible material with potassium chlorate must be made with the minutest precautions, as the least shock or friction may cause an explosion."

Davis[8] says that "Many chlorate mixtures, particularly those which contain sulfur, sulfides and picric acid, are extremely sensitive to blow and friction.***."

According to Dupre,[9] " All chlorate mixtures are liable to what is termed spontaneous ignition or explosion in the presence of a variety of materials, more particularly of such as are acid, or are liable to generate acid; and all chlorate mixtures are readily exploded by percussion, such as a glancing blow, which might easily and would often occur in charging a hole."

The chlorates are salts of chloric acid and are easily replaced from their compounds by stronger acids. This reduces the stability of chlorate mixtures in which traces of strong acids may be encountered. A drop of sulfuric acid placed on a combustible mixture containing chlorate usually results in deflagration.

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[5] U. S. Patents 243,432 and 243,433.

[6] Mémorial des poudres et saltpêtres XV, p. 181.

[7] Gody, L., Traité théorique et pratique des matières explosives: 3d ed., 1907, p. 240. See, also, Howell, S. P., Sensitiveness of Explosives to Frictional Impact: Bureau of Mines Tech. Paper 234, 1919, p. 6.

[8] Davis, T. L., The Chemistry of Powder and Explosives: John Wiley & Sons, New York, 1943, vol. 2, pp. 358, 359.

[9] DeKalb, C., Manual of Explosives: 1900, p. 16.

Combustible chlorate mixtures are much more sensitive to friction than mixtures in which the chlorate is replaced by other oxidants,[10] such as nitrate, and many serious accidents have occurred because of this extreme friction sensitivity. Howell[10/] showed that a chlorate explosive being used in the United States for mining, which had given premature explosions, could, in mixture with coal dust and pyrites, be detonated by moving a copper needle within the mixture.

The quotation from Guttmann[3/] above refers to a disaster in one of the first attempts to use chlorates as a major constituent of explosives. More details are given by Marshall.[11/]

CHLORATES AND PERCHLORATES ARE NOT USED AS MAJOR INGREDIENTS IN PERMISSIBLE EXPLOSIVES BUT ARE USED IN PYROTECHNIC COMPOSITIONS

The Bureau of Mines early recognized the danger existing in employing chlorate explosives. As a matter of policy, it does not test for use in mines any explosive containing chlorate or perchlorates as a major ingredient.

However, because the chlorates may be produced cheaply from the chlorides, and in some compositions are more suitable than other oxidizers for the effect desired, they have been used extensively in pyrotechnic compositions. All who manufacture or handle such explosives should be made aware of the danger. A great deal has been written on the subject, and much experience has been obtained with some of these mixtures.

Experience alone is not always a safe index to sound practice. In one accident investigated by this Bureau, one man was killed and two women in an adjacent building were injured by the detonation of a sulfur-potassium chlorate composition in the process of being mixed, although it was stated that the mixing operation involved had been in use in that plant for 20 years without mishap. There is, of course, the possibility that the raw material used at the time of the accident may have been different from that upon which past experience was based. Thus, if the particular lot of sulfur employed were acid, abnormal sensitivity of the chlorate-containing mixture might result. In any event, safe experience, even for 20 years, would not justify

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10/ Howell, S. P., Sensitiveness of Explosives to Frictional Impact: Bureau of Mines Tech. Paper 234, 1919, pp. 12-15.

11/ Marshall, A., Explosives: Vol. 1, 1917, p. 35.

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a practice that exposed the mix operator and others. Instead, the hazards should be recognized and isolation and remote control provided.

With the advent of cheap electricity, many compounds previously produced only with difficulty or at high cost are now capable of commercial production by electrolytic means. Among these are the perchlorates, particularly those of sodium and potassium. These salts contain a greater percentage of available oxygen than do the corresponding chlorates and have the advantage over the chlorates of greater stability. The perchlorates, unlike the chlorates, are salts of a strong acid that is not broken down by other acids. Recent pyrotechnic formulas have favored perchlorates instead of chlorates.

COMMENTS ON THE SENSITIVITY OF PERCHLORATE MIXTURES

Because of the advantages of perchlorates over chlorates, much literature has appeared that would make the perchlorates seem safer in combination with organic or combustible material.

Davis[12] says "The perchlorates are intrinsically more stable and less reactive than the chlorates, and are much safer in contact with combustible substances."

Marshall[13] holds that "The perchlorates possess the advantage over the chlorates that they are more stable and less sensitive ***."

Potassium and ammonium perchlorate mining explosives have been permitted to be used in the mines of England and Belgium and in other countries. As noted above, in the United States, explosives containing chlorates or perchlorates as a major ingredient are not accepted for tests. Howell found, in developing the Bureau of Mines pendulum-friction device, that, of all the samples tested at that time, the only ones failing the fiber shoe contained either a chlorate or a perchlorate.[14]

In the past few years there has been a definite trend toward the replacement of potassium chlorate in many mixtures with potassium perchlorate on the assumption that the perchlorate mixture was less hazardous because the perchlorate was so much more stable and would not be influenced by the presence of acids.

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[12] See footnote 8.
[13] Marshall, A., op. cit., p. 383.
[14] See footnote 10.

According to Weingart,[15]

> Barium and strontium nitrates, aluminum, and similar substances in combinations with potassium perchlorate have been found to be among the safe mixtures even when mixed with sulphur and gums.***. Aluminum powder in mixtures with potassium chlorate, barium nitrate and shellac or other carbon sources are classed as hazardous.

Such a statement would seem to indicate that by merely replacing the potassium chlorate in the above mixture with potassium perchlorate, the hazard has been greatly reduced.

TESTS ON MIXTURES CONTAINING PERCHLORATE - IMPACT AND STATIC-SPARK SENSITIVITIES OF MIXTURES CONTAINING PERCHLORATES

Early in 1944 there was brought to the attention of the Explosives Division of the Bureau of Mines an accident that had occurred in the process of manufacture of practice land mines in which some of the mines had exploded, killing several persons. Investigation of this accident disclosed that the powder they contained was a mixture that, when reviewed in the light of the above quotation of Weingart, might be thought safe.

As this accident aroused considerable interest, it was decided to make a few tests to determine how sensitive the composition was. The results were startling. When subjected to the Bureau of Mines' standard pendulum friction test,[16] the material detonated so severely on the first trial with the fiber shoe that the tests had to be discontinued for fear of injuring the apparatus.

The sample was then tested with the pressure friction apparatus. This consists essentially of a cylindrical brass plunger that exerts a fixed pressure and rotates at a fixed speed upon a small weight of the sample contained in a brass cup. Only materials exceedingly sensitive to friction, such as the initiating explosives, will fire in this test. The mixture ignited during the test and was found to have a friction sensitivity slightly less than that of mercury fulminate.

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[15] Weingart, G. W., Pyrotechny: Chemical Publishing Co., New York, 1939, p. 25.

[16] For a description of this test, see Bureau of Mines Bull. 346, by J. E. Tiffany and C. E. Munroe.

When tested for its sensitivity to static spark, it was found that at 5,000 volts only 0.007 joule spark energy was required for ignition, an energy only one-tenth that necessary to initiate mercury fulminate. That initiation by such a low energy spark constitutes an important hazard can be appreciated when it is understood that a static charge energy of 0.015 joule may be built upon and discharged from the human body under conditions that are not too stringent. These tests show that this mixture is far from safe; instead, it is as hazardous as mercury fulminate, a compound known to be dangerous and one that should always be handled with the greatest precaution.

In the last two years, other perchlorate mixtures have been shown to be hazardous. During this time at least three separate industrial accidents involving a photoflash composition containing potassium perchlorate together with aluminum and magnesium powders have been brought to the attention of the Bureau of Mines. In these explosions, five men were killed and two injured.

Recently, the Bureau has tested several mixtures containing potassium perchlorate mixed with nickel, titanium, and infusorial earth. The explosions of some of these mixtures when being tested with the fiber shoe on the pendulum friction device were so severe that the weight of test sample was reduced from the standard 7 grams to 2 grams. Even with this reduction in sample weight, four of six mixtures tested failed to pass the fiber-shoe test, showing that they were hazardous where friction may be encountered.

On determining the static spark sensitivity, all the mixtures tested when confined required less energy to ignite them than can be built upon and discharged from the human body; the energies ranged from 0.0012 to 0.0062 joule. When unconfined, the necessary energy for ignition ranged from 0.0012 to 0.012 joule, these energies still being less than that capable of being discharged from the human body. All such mixtures must be considered dangerous.

From the foregoing discussion it should be clear that although the perchlorates are undoubtedly more stable than the corresponding chlorates and are not so subject to the dangers from the presence of free acids as are the chlorates, it should not be assumed that all perchlorate mixtures are safe. Although it may be true in many instances that mixtures containing chlorates may be initiated more easily than the similar mixture in which the chlorate is replaced by the corresponding perchlorate, yet the perchlorate mixture may still be initiated by friction, impact, or spark at energies that cannot be considered safe. Indeed, as the above examples show, a number of these must be considered to be extremely dangerous.

Before a perchlorate mixture is accepted, it should be tested thoroughly.

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